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(Annual Summary)

KINETICS OF SYNTHESIS AND DECOMPOSITION REACTIONS
OF IONIC COMPOUNDS CONTAINING N-F CATIONS

February 1, 1971 through January 31, 1972

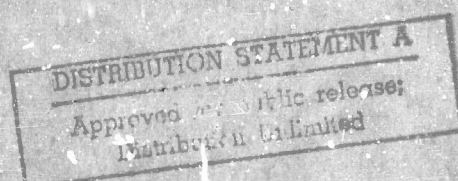
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IITRI Project C6140

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13. ABSTRACT Kinetic studies indicate that NF_4AsF_6 decomposes via an equilibrium dissociation $\text{NF}_4\text{AsF}_6 = \text{NF}_5 + \text{AsF}_5$ followed by a rapid fractional order reaction: $\text{NF}_5 = \text{NF}_3 + \text{F}_2$ Attempts to identify NF_5 in the decomposition products were inconclusive. The first phase of this work has been submitted for publication. The reaction of bromine dioxide (probably containing some BrO_2) with O_2F_2 yields bromine pentafluoride if the oxygen fluoride is in excess, but at smaller ratios bromine oxyfluorides are produced. The stoichiometry of these reactions is being investigated. Several samples of NH_3FClO_4 were prepared from N-fluoriosopropyl carbamate and perchloric acid. Two of the samples exploded violently during solvent removal.			

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Matrix isolation						
Infrared spectra						
Bromine oxides						
Bromine oxyfluorides						

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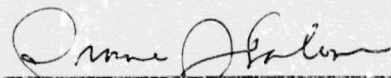
FOREWORD

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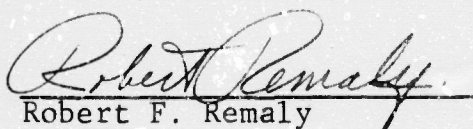
This is the fourth annual report on IITRI Project C6140, Contract No. N00014-68-C-0279, entitled, "Kinetics of Synthesis and Decomposition Reactions of Ionic Complexes Containing N-F Cations." This research was supported by the Office of Naval Research, Power Branch, with Mr. Richard L. Hanson as Scientific Officer, until May 31, 1971 and Mr. Roland D. Jackel after that date. The report covers the period from February 1, 1971 through January 31, 1972. The work has been extended for an additional year. We wish to thank Drs. H. Hyman, I. Sheft, and E. Appelman of the Argonne National Laboratory for their valuable suggestions regarding the research. We also wish to thank Dr. Alan Snelson, of IITRI, who conducted the matrix isolation phase of this program.

Respectfully submitted,

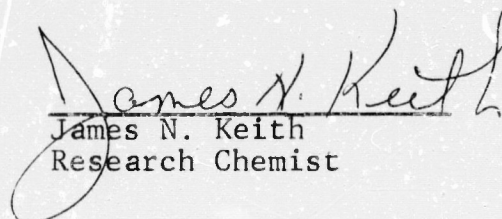
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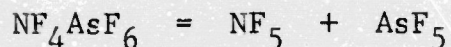
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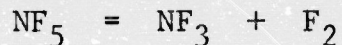
ABSTRACT

KINETICS OF SYNTHESIS AND DECOMPOSITION REACTIONS OF IONIC COMPOUNDS CONTAINING N-F CATIONS

Kinetic studies indicate that NF_4AsF_6 decomposes via an equilibrium dissociation



followed by a rapid fractional order reaction:



Attempts to identify NF_5 in the decomposition products were inconclusive. The first phase of this work has been submitted for publication.

The reaction of bromine dioxide (probably containing some BrO_3) with O_2F_2 yields bromine pentafluoride if the oxygen fluoride is in excess, but at smaller ratios bromine oxyfluorides are produced. The stoichiometry of these reactions is being investigated.

Several samples of NH_3FClO_4 were prepared from N-fluoriosopropyl carbamate and perchloric acid. Two of the samples exploded violently during solvent removal.

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KINETICS OF THE SYNTHESIS AND DECOMPOSITION REACTIONS OF IONIC COMPOUNDS CONTAINING N-F CATIONS

1. INTRODUCTION

The purpose of the present research is the study of the properties of NF_4^+ salts, especially the mechanism of decomposition, and synthesis and examination of certain perbromates, and the study of other heptavalent bromine compounds. The study of higher-valent bromine compounds has also led us to a closer examination of the bromine oxides, and their reaction with oxygen fluorides.

During the year, after consultation with Mr. Hanson, an additional effort was included, consisting of the synthesis of fluorammonium perchlorate, NH_3FClO_4 for use in molecular beam experiments in collaboration with Dr. John B. Fenn at Yale University.

2. RESULTS AND DISCUSSION

2.1 Decomposition of NF_4AsF_6

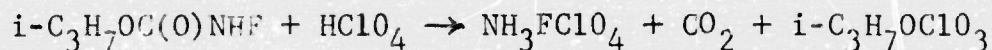
Our work on this compound has been summarized in the form of a paper, and submitted for publication in the Journal of Fluorine Chemistry. A copy of this paper is included in this report as an appendix, and therefore the work will not be discussed in the text of this report.

2.2 Synthesis of Fluorammonium Perchlorate

During the course of this program, the suggestion was made by Mr. Hanson that fluorammonium perchlorate, NH_3FClO_4 might be of particular interest to us since it contains a fluorinated cation of a base which has never been isolated. Using molecular beam experiments, Dr. John B. Fenn, Yale University, has identified ammonia and perchloric acid as the gaseous species in the vaporization of ammonium perchlorate. Thus, one might hope

to identify fluoramine from the perchlorate in a similar manner. We therefore undertook the task of preparing a sample for these experiments, and planned to attempt a matrix isolation experiment as well.

Fluorammonium perchlorate has been prepared by the reaction of anhydrous perchloric acid with N-fluoro isopropyl carbamate:



The latter compound was obtained² by aqueous fluorination of i-propyl carbamate.

The N-fluorocarbamate was prepared using this method and isolated by vacuum distillation. The purity was monitored by proton nmr, and only material containing no detectable organic impurities was used in the next step. Perchloric acid was prepared according to the method of G. F. Smith,³ and used within 24 hrs. of distillation. It was usually very pale yellow.

Two preparations of fluorammonium perchlorate exploded violently during transfer and drying, however, one sample was obtained in a dry, powdered state. But, while waiting for the matrix isolation experiment for several days, hydrolysis occurred, and the product became visibly wet. In all three preparations care was taken to use the purest possible fluorocarbamate, and the perchloric acid was used as soon after preparation as possible. Although care was taken to wash the solid carefully, a small amount of residual i-propyl perchlorate or excess perchloric acid remained on the solid. More likely, even a very minute quantity of chlorine oxide in the perchloric acid may be sufficient to initiate decomposition. In any case, since this was not the main objective of our work, it was dropped by agreement with Mr. Jackel and our attention was returned to bromine oxyfluorides.

2.3 Bromine Oxyfluorides and Oxides

Heptavalent bromine is now known in two forms: the perbromates, obtained by Appelman by aqueous fluorination of bromates,⁴ and perbromyl fluoride,⁵ from fluorination of KBrO_4 in HF . To date this is the only known method for preparation of perbromyl fluoride.

Despite several attempts to prepare bromine heptafluoride by direct or indirect fluorination of lower fluorides and salts, no evidence of the existence of other heptavalent bromine compounds is presently available. It is very likely, judging from the chemistry of the higher valence states of the transition metals, that the oxyfluorides will be more stable than the fluorides. Since the oxyfluorides are expected to be reactive and of limited stability at ordinary temperatures, we are studying the low-temperature fluorination of bromine oxides by oxygen fluorides.

The tedious procedure involved in the synthesis of perbromates induced us to look more closely at the bromine oxides, which have been briefly characterized, but not studied in much detail.⁶⁻⁸ It seems an obvious approach to prepare bromine oxyfluorides by direct fluorination of the oxides. Since their instability makes it necessary in any case to use low temperatures, the use of dioxygen difluoride seems especially suitable here. Bromine dioxide has been fluorinated by fluorine and by BrF_5 to bromyl fluoride,⁹ BrO_2F . Dioxygen difluoride will surely effect the same reaction at a lower temperature, and also should produce perbromyl fluoride, BrO_3F , from BrO_3 . It is also hoped that other heptavalent oxyfluorides will be produced, such as BrO_2F_3 or BrOF_5 .

We have therefore initiated a study of the reactions of the bromine oxides with the oxygen fluorides. The synthesis and analysis of bromine dioxide and some preliminary experiments on its reaction with dioxygen difluoride was reported

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previously.¹⁰ At that time the only identifiable fluorine - containing product of a reaction at -126°C with an unmeasured quantity of O_2F_2 was bromine pentafluoride, although a less volatile material was also present which is now believed to have been bromyl fluoride.

Later experiments on $\text{BrO}_2/\text{BrO}_3$ mixtures with less O_2F_2 have indicated that bromyl and possibly some perbromyl fluoride were produced. Thus, BrO_2 was prepared at -183°C using a 6:1 O_2/Br_2 mixture. The product was mostly yellow, but white on the upper surfaces. After evaporation of the excess bromine at -30°C , it was determined that 15.3 cc of bromine had been consumed, corresponding to 30.6 cc BrO_2 . A previously prepared sample of O_2F_2 was distilled in, and the reactor brought to -126°C for 90 min. Most of the color disappeared, and the reactor was coated with white solid with a small spot of pale yellow-orange color. At the end of this time the volatile product consisted of 34.1 cc O_2 and a trace of F_2 .

On thawing to -78°C a further 17.6 cc O_2 , 1.5 cc F_2 and 9.9 cc of condensible gas were obtained. The infrared spectrum of the condensible gas appeared to be mainly that of a mixture of fluorocarbons and SiF_4 , with three smaller peaks (960, 875, and 590 cm^{-1}) which may be due to BrO_3F (976.5, 875.5, and 606 cm^{-1} , for the three strongest peaks¹¹). Overnight these peaks disappeared, and the color of bromine appeared. Aside from the appearance of a small new peak at 1280 cm^{-1} , the spectrum was otherwise unchanged.

The -78° residue did not appear to distill at room temperature, but melted to a clear colorless liquid which bubbled slowly, producing (overnight): 36.4 cc O_2 , 14.2 cc Br_2 , and 10.0 cc SiF_4 (IR spectrum). Using the SiF_4 value to calculate the fluorine, and to correct the oxygen value, this becomes: 26.4 cc O_2 , 14.2 cc Br_2 and 20.0 cc F_2 , corresponding very roughly to the composition BrO_2F .

The mass balance is incomplete due to uncertainty about the nature of the condensible products obtained at -78°C , and the oxygen values seem excessively high. In future experiments attempts will be made to obtain a mass balance by measuring the amount of O_2F_2 , fractionating the condensible material, and avoiding contact with stopcock grease as much as possible.

Work is also in progress on bromine tioxide, BrO_3 . This interesting compound can be prepared only at higher temperatures, best at 0°C , where it is stable only in the presence of ozone. To date, poor yields have prevented much progress with this compound, but larger samples should be obtainable with a new, thin-walled reactor under construction. When larger samples are available, the reaction with O_2F_2 and the hydrolysis of BrO_3 are planned. It is expected that fluorination will yield BrO_3F and the BrO_3 will hydrolyze to a mixture containing bromate and perbromate ions.

3. FUTURE WORK

3.1 Heptavalent Bromine

Work will continue during 1972 on the synthesis and reactions of BrO_3 , directed at preparing BrO_3F and HBrO_4 by this new route and at preparing new oxyfluorides. At the same time, the reaction of BrO_2 with O_2F_2 and O_4F_2 will be examined closely to determine if oxyfluorides higher than BrO_2F are obtainable by this method.

It may be worthwhile at this point to examine the reactions of O_2F_2 with the bromine fluorides. Von Grosse's " O_2BrF_5 " should be re-examined to see if any evidence can be found for the existence of an oxyfluoride in this reaction.¹² It is expected, however, that the major effort in this area will be with the bromine oxides.

3.2 The Dichlorofluoronium Cation Cl_2F^+

As described in our recent proposal, work will be initiated this year on the decomposition of the interesting new salt,^{13,14} $\text{Cl}_2\text{F}^+\text{AsF}_6^-$. This salt is at least formally related to the "base" Cl_2F_2 , which, if it exists, would be the dimer of chlorine monofluoride. No such dimer has yet been established, although the Trouton's constant,¹⁵ 28.0, may suggest association. This is taken from old data, however, and could indicate nothing more than the presence of ClF_3 as an impurity.

We plan to examine the infrared spectrum of the decomposition products of Cl_2FAsF_6 by matrix isolation techniques, as well as that of chlorine monofluoride. Vapor pressure measurements of a carefully purified sample of ClF should also yield a more reliable Trouton's constant.

Work on this problem will probably be initiated during the second quarter of the program.

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APPENDIX

THE DECOMPOSITION OF NF_4AsF_6

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Submitted to
Journal of Fluorine Chemistry

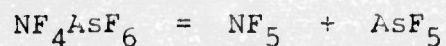
THE DECOMPOSITION OF NF_4AsF_6

SUMMARY

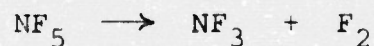
NF_4AsF_6 decomposes smoothly at 175°C and above, to the starting materials NF_3 , F_2 and AsF_5 . The decomposition has been followed by total pressure measurements, and found to obey the equation

$$P^{3/2} = At + B$$

This has been interpreted in terms of an equilibrium dissociation step:



followed by irreversible decomposition of the unstable NF_5 :



The latter step is taken to be a 3/2-order reaction:

$$\frac{dP}{dt} = k_1 P_n P_a^{1/2}$$

where P_n is the partial pressure of NF_5 and P_a that of AsF_5 . Taking the equilibrium into

account, the above equation is integrated to yield:

$$P_a^{3/2} - (P_a^0)^{3/2} = 3k_1K_{eq}t/2$$

An attempt to identify NF_5 in the products by matrix isolation methods yielded, besides the expected NF_3 and AsF_5 , an unknown minor product which appeared not to contain nitrogen.

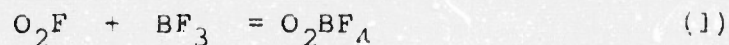
THE DECOMPOSITION OF NF_4AsF_6

by

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INTRODUCTION

The stability of the recently reported tetrafluoroammonium salts^{1,2} is quite remarkable in view of the low basicity of difluoramine^{3,4} and the absence of detectable basic properties in nitrogen trifluoride.⁴ The existence of such salts is particularly interesting since the conjugate base, nitrogen pentafluoride, is not known, and is expected to be extremely unstable. The case is analogous to that of the dioxygenyl salts, such as O_2BF_4 , which have been shown⁵ to be derived from the very unstable base O_2F :



We thus have stable salts of very unstable bases, which can be prepared only by the use of forcing conditions, such as glow discharge or high pressure methods.

As in the case of the dioxygenyl salts, neither synthetic route is conducive to kinetic studies, but it is possible to obtain some kinetic information on the thermal decomposition by pressure measurements. As with O_2BF_4 , the kinetic data indicated the existence of an equilibrium dissociation which controls the rate of decomposition.

Attempts were made to obtain infrared spectra of primary dissociation products by matrix isolation techniques, but it was not possible to draw definite conclusions.

EXPERIMENTAL

Materials and Equipment: All synthetic work and the kinetic and isotopic exchange studies were performed in metal vacuum lines of the type used for reactive fluorine compounds. Transfers of solid NF_4AsF_6 were made in a nitrogen-filled drybox.

Nitrogen trifluoride was purchased from Air Products and Chemicals, Inc. and arsenic pentafluoride from Ozark-Mahoning Co. Fluorine (Matheson Co.) was passed through sodium fluoride prior to use. Isotopically enriched nitrogen (95% ^{15}N , Merck Sharpe and Dhome) was

fluorinated in a glow discharge reaction⁶ at -196°C to form $^{15}\text{NF}_3$.

Preparation of NF_4AsF_6 : NF_4AsF_6 was prepared in a glow discharge reaction at -80°C, using a reactant ratio of $\text{F}_2:\text{NF}_3:\text{AsF}_5=1.5:1:1$. The Pyrex glow discharge tube was evacuated and removed from the vacuum line by sealing the connecting tubing and opened in a dry-box to transfer the contents. Analysis of the thermal decomposition products indicated the presence of NF_3 , F_2 and AsF_5 in equal amounts. Hydrolysis produced a 2:1 mixture of NF_3 and O_2 .

Kinetic Measurements: The thermal decomposition of NF_4AsF_6 was followed by measurement of the total pressure in a passivated 100 cc Monel cylinder by means of a Wallace-Tiernan FA145-780 vacuum gauge. The cylinder was heated with a 1650 watt, 4 x 12 in. Lindberg Hevi-Duty tube furnace, using a copper-constantan control thermocouple. A record of the temperature of the sample (by means of a thermocouple taped directly to the cylinder) was kept on a Varian millivolt recorder.

Infrared Spectra: The infrared spectra of the starting materials and of the decomposition products were recorded using a Perkin-Elmer Model 621 Grating Spectrophotometer. Conventional matrix isolation equipment was used, consisting of a cesium iodide window mounted in a copper block attached to a cold finger which can be rotated to position the window. The Dewar was of metal construction, the outer jacket being filled with liquid nitrogen, surrounding the liquid helium-filled cold finger. The furnace consisted of a 1/8 x 1 in. platinum tube heated by induction. The temperature was measured by means of a thermocouple.

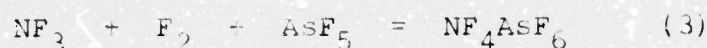
RESULTS AND DISCUSSION

As in the similar case of $O_2B^+F_4^-$, the rate of decomposition of NF_4AsF_6 in a sealed container decreases steadily during the reaction, and the initial rate is restored upon removal of the decomposition products by evacuation. The data are well represented by the equation:

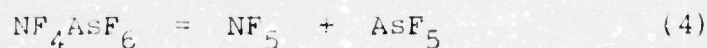
$$P^{3/2} = At + B \quad (2)$$

The parameters of this equation were computed by the Method of Least Squares, using a Hewlett-Packard Model 9100B electronic calculator. The data are presented in Tables 1-7.

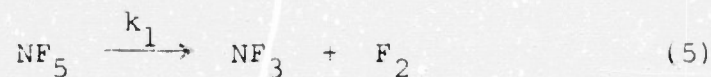
It is evident that an equilibrium step is involved in the decomposition reaction, just as with the dioxygenyl salts. It is extremely unlikely that the synthetic reaction



is involved here considering the rather extreme conditions required for this reaction. It is more likely that an equilibrium dissociation step is involved.



This is followed by decomposition of the unstable NF_5



The form of Equation 2 indicated that this step must be considerably more complex than indicated by Equation 5. A $3/2$ order reaction will produce the correct results:

$$\frac{dP}{dt} = k_1 P_n P_a^{1/2} \quad (6)$$

Table 1
 DECOMPOSITION OF NF_4AsF_6
 AT 175°

Time, min.	Total Pressure, mm.	
	obs.	calcd.
0 0	0 0	0.0
2 8	0 7	0.7
11 2	1 3	1.3
16.9	1.7	1.6
27.2	2.2	2.2
38.4	2.7	2.7
64.7	3.7	3.7
127.0	5.7	5.7

Table 2
DECOMPOSITION OF NF_4AsF_6
AT 195°

Time min.	Total Pressure, mm.	
	obs	calcd.
0.0	0.3	1.1
0.5	0.7	1.4
2.1	1.7	2.1
4.1	2.7	2.8
6.9	3.7	3.7
10.0	4.7	4.5
13.7	5.7	5.5
18.4	6.7	6.6
32.8	9.7	9.5
45.0	11.7	11.6
57.8	13	13.6
78.7	16.7	16.7
93.3	18.7	18.7
126.7	22.7	22.8

Table 3
DECOMPOSITION OF NF_4AsF_6
AT 205°

Time, min.	Total Pressure, mm.	
	obs.	calcd.
0.0	0.3	1.3
0.2	0.7	1.6
1.0	1.7	2.3
2.0	2.7	3.1
4.5	4.7	4.8
6.2	5.7	5.8
12.1	8.7	8.7
14.1	9.7	9.5
27.3	14.7	14.6
36.4	17.7	17.6
42.4	19.7	19.4
49.3	21.7	21.4
60.3	24.7	24.5
80.8	29.7	29.7
93.6	32.7	32.7
102.8	34.7	34.8
131.7	40.7	41.0

Table 4

DECOMPOSITION OF NF_4AsF_6
AT 218.5°

Time, min.	Total Pressure, mm.	
	obs.	calcd.
0.0	0.6	4.8
1.1	4.7	7.2
3.1	9.7	10.8
5.9	14.7	14.9
10.8	21.7	21.1
15.0	26.7	25.7
18.6	30.7	29.4
22.5	34.7	33.1
31.5	42.7	40.9
40.7	49.7	48.3
47.5	54.7	53.4
54.7	59.7	58.5
64.5	65.7	65.1
71.0	69.7	69.4
80.0	74.7	75.0
89.9	79.7	81.0
100.2	84.7	87.0

Table 5
DECOMPOSITION OF NF_4AsF_6
AT 222°

Time, min.	Total Pressure, mm.	
	obs	calcd.
0.0	0.6	5.2
1.0	5.7	7.8
2.1	8.7	10.0
4.6	14.7	14.2
7.3	19.7	18.9
10.5	24.7	23.4
14.2	29.7	28.1
18.2	34.7	32.8
28.0	44.7	43.0
34.8	50.7	49.4
39.6	54.7	53.7
46.0	59.7	59.2
52.8	64.7	64.8
59.6	69.7	70.1
67.5	74.7	76.0
75.6	79.7	81.9

Table 6
 DECOMPOSITION OF NF_4AsF_6
 AT 222°
 IN PRESENCE OF AsF_5

Time, min.	Total Pressure, mm.	
	obs.	calcd.
0.0	99.0	99.5
24.9	107.7	108.3
30.9	110.0	110.1
43.9	115.0	114.9
57.0	120.0	119.4
85.7	130.0	129.2
114.6	140.0	138.9
180.0	161.0	160.3
240.0	178.6	179.4

Table 7
 DECOMPOSITION OF NF_4AsF_6
 AT 222°
 IN PRESENCE OF NF_3

Time min.	Total Pressure, mm.	
	obs.	calcd.
0.0	111.5	110.4
4.3	113.0	112.6
7.4	114.0	114.0
9.9	115.0	115.2
12.2	116.0	116.2
17.2	118.0	118.3
22.3	120.0	120.3
27.7	122.0	122.4
35.5	125.0	125.2
44.0	128.0	128.2
58.7	133.0	132.9
71.5	137.0	136.8
84.3	141.0	140.5
100.3	145.0	144.9
131.9	153.0	153.1

where $P_n = \text{NF}_5$ pressure and $P_a = \text{AsF}_5$ pressure.

Since P_n is controlled by the equilibrium,

$P_n = K_{eq}/P_a$ and:

$$\frac{dP}{dt} = k_1 K_{eq} P_a^{-1/2} \quad (7)$$

Taking $dP = dP_a$, and integrating:

$$P_a^{3/2} - (P_a^0)^{3/2} = \frac{3}{2} k_1 K_{eq} t \quad (8)$$

In terms of the experimental quantities:

$$\frac{\sqrt{3}}{9} (P_T + 2P_a^0)^{3/2} - (P_a^0)^{3/2} = \frac{3}{2} k_1 K_{eq} t \quad (9)$$

except for the experiment in which NF_3 was added.

$$\frac{\sqrt{3}}{9} (P_T - P_c)^{3/2} - (P_a^0)^{3/2} = \frac{3}{2} k_1 K_{eq} t \quad (10)$$

where P_c is the calculated partial pressure due to the NF_3 added at the beginning of the experiment, and P_T is the total pressure.

The rate constant cannot be determined separately from the equilibrium constant. The products of the constants $k_1 K_{eq}$, presented in Table 8, can be computed from the slopes of $(P_T + 2P_a^0)^{3/2}$ or $(P_T - P_c)^{3/2}$ versus t . An Arrhenius plot of these products yields, for the sum of the overall heat of sublimation

Table 8
KINETIC CONSTANTS

Temperature, °C	$10^6 k_1 K_{eq}^*$	
	obs	calcd.
175	3.78	3.79
195	28.5	27.5
205	64.1	69.6
218.5	248	230
222	296	309
222 (AsF ₅)	281	309
222 (NF ₃)	85.1	309

* $\text{Mole}^{3/2} \text{liter}^{-3/2} \text{sec}^{-1}$.

and the activation energy for the decomposition of NF_5 , a value of 41 kcal/mole.

In an attempt to obtain support for the postulate that NF_5 is present as an intermediate, matrix isolation studies were performed with NF_4AsF_6 .

Reference spectra of NF_3 and AsF_5 were obtained, and compared with the literature.^{7,8} The spectra were in satisfactory agreement, and no evidence of significant impurities was seen. Several runs were made with NF_4AsF_6 , decomposing at different temperatures. The results are shown in Table 9.

In the experiments which produced strong spectra, new peaks were observed at 1043, 823, 332, and 309 cm^{-1} , which did not appear to be due to overtones, matrix effects, etc. A search of the literature did not disclose a likely impurity to which these peaks could be attributed.

Examination of the spectra of the products from $^{15}\text{NF}_4\text{AsF}_6$, however, revealed the presence of the same new peaks, with the same relative intensities. The fact that no isotopic shift is observed indicates that the source of these

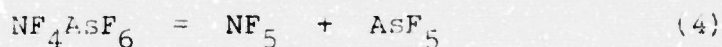
Table 9
INFRARED SPECTRA IN NEON MATRIX

Frequency, cm^{-1}				
$^{14}\text{NF}_4\text{AsF}_6$	$^{15}\text{NF}_4\text{AsF}_6$	$^{14}\text{NF}_3$	$^{15}\text{NF}_3$	AsF_5
1049	1043			
1027	1026	1027	1027	
	1003.5			1004
899	898.5	899	899	
	878.5			878
827	822.5			
809	808			809
782	782			782.5
		642	638	
489		490	489	
398	397.5			398
367	367			367
332	331			
309	307			

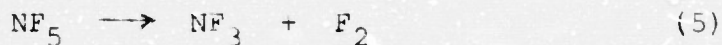
peaks is not a nitrogen compound derived from the NF_4AsF_6 , but an impurity common to the two samples or resulting from interaction of the decomposition products with the materials of the apparatus. We have not been able to identify this impurity, nor has any evidence of NF_5 been found.

CONCLUSIONS

NF_4AsF_6 decomposes smoothly above 175°C at a rate which decreases as the reaction proceeds, in a manner similar to that of O_2BF_4 . The data can be correlated with a mechanism consisting of an equilibrium dissociation:



followed by decomposition of NF_5



This process must be somewhat more complex than indicated above, since the data indicate that the overall order is $3/2$. A process which is first order in NF_5 and $1/2$ order in AsF_5 will fit the data

$$\frac{dp}{dt} = k_1 P_n P_a^{1/2} \quad (6)$$

The implication of this mechanism, that NF_5 exists as an intermediate in this process, was not supported by matrix isolation studies. It would be expected, however, to be very unstable, and to have only transitory existence.

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